### COMPONENTS:

- (1) Mercury; Hg; [7439-97-6]
- (2) Alcohols

**EVALUATOR:** 

H. Lawrence Clever Chemistry Department Emory University Atlanta, Georgia 30322 USA

1985, August

### CRITICAL EVALUATION:

An Evaluation of the Solubility of Mercury in Alcohols.

There are measurements of the solubility of mercury in only two alcohols. They are methanol and 2-propanol. The systems are discussed below.

### Mercury + Methanol

Reichardt and Bonhoeffer (ref. 1) measured the solubility at 313.15 and 336.15 K, Kuntz and Mains (ref. 2) at 298.15 K, and Spencer and Voigt (ref. 3) at five temperatures between 288.15 and 308.15 K. Three quite different methods were used: an amalgamation method, a spectroscopic method and a radioactive tracer method.

Figure 1 show the mole fraction solubilities on a  $\ln x_1$  vs. 1000/(T/K) plot. The Kuntz and Mains (ref. 2) value was obtained assuming the mercury extinction coefficient is the same in a hydrocarbon and methanol. As the authors mention, this is a poor assumption and may be the reason for the apparent low value. The extinction coefficient was obtained by the spectroscopic measurement of a mercury saturated hexane solution assuming the solubility value of mercury in hexane of Moser and Voigt (ref. 4) was correct. The Reichardt and Bonhoeffer values were obtained by a method that has not been thoroughly tested as some other methods. The dotted line of Figure 1 is the linear regression line for all of the data. The solid line is for the Spencer and Voigt (ref. 3) data only. We have arbitrarily chosen to use the Spencer and Voigt data only as the basis for the tentative values.

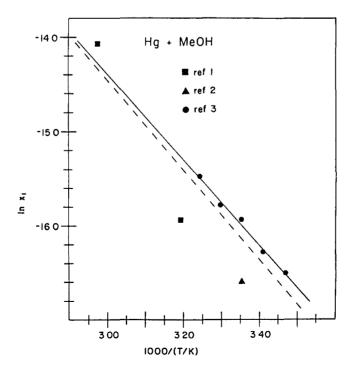


Figure 1. The solubility of mercury in methanol. In  $x_1$  vs. 1000/(T/K)

The Spencer and Voigt data in units of concentration, mole fraction and molality were treated by linear regression to obtain the constants of Table 1. Table 2 contains the smoothed tentative solubility values and the thermodynamic changes for the transfer of one mole of mercury from liquid metal to the hypothetical unit concentration solution.

Table 1. Mercury + Methanol. Linear regression for the equation  $\ln(\text{soly})$ = A(1) + A(2)/(T/100 K).

Solubility	A(1) ± Error	A(2) ± Error	Std. Error about the Regression Line
c <sub>1</sub> /mol dm <sup>-3</sup>	$2.3763 \pm 0.7650$	-45.1788 + 2.2789	$1.2 \times 10^{-7}$
x -	$-0.7753 \pm 0.8625$	$-45.3539 \pm 2.5693$	5.7 x 10 -•
$m_1^2/\text{mol kg}^{-1}$	$3.0153 \pm 0.6046$	$-46.3685 \pm 1.8012$	1.3 x 10 -7

Table 2. The solubility of mercury in methanol. Tentative values of the solubility in concentration, mole fraction and molality as a function of temperature at 0.1 MPa and thermodynamic changes.

Temperature		Mercury Solubility		
t/°C	T/K	Concentration 10°c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction 10°x <sub>1</sub>	Molality 10°m <sub>1</sub> /mol kg <sup>-1</sup>
15	288.15	1.7	6.7	2.1
20	293.15	2.2	8.8	2.8
25	298.15	2.8	11.4	3.6
30	303.15	3.6	14.7	4.6
35	308.15	4.6	18.7	6.0
40	313.15	5.8	23.6	7.6
50	323.15	9.1	37.0	12.0
60	333.15	13.9	56.4	18.4
ΔΗ <sub>1</sub> α		37.6 <u>+</u> 1.9	37.7 ± 2.1	38.6 <u>+</u> 1.5
$\Delta s_1^{\mathbf{b}}$		19.8 <u>+</u> 6.4	$-6.4 \pm 7.2$	25.1 ± 5.0

a units kJ mol -1 b units J K -1 mol -1

### Mercury + 2-Propanol

Only Spencer and Voigt (ref. 3) report the solubility of mercury in 2-propanol. Their data, classed as tentative, were treated by linear regression in the units of concentration, mole fraction and molality. The regression constants are in Table 3 and the smoothed data and thermodynamic changes are in Table 4.

The enthalpy changes are the same within experimental error for the solution of mercury in methanol and 2-propanol. The mole fraction solubility of mercury in methanol is only about one-tenth of the solubility in an alkane, but it is 22 times more soluble than in water.

Table 3. Mercury + 2-Propanol. Linear regression for the equation ln(soly) = A(1) + A(2)/(T/100 K).

Solubility	A(1) <u>+</u> Error	A(2) ± Error	Std. Error about the Regression Line
c <sub>1</sub> /mol dm <sup>-1</sup>	1.8159 ± 0.1402 -0.4575 + 0.1901	$-43.6772 \pm 0.4175$ $-44.5711 \pm 0.5665$	1.7 x 10 <sup>-8</sup> 1.6 x 10 <sup>-8</sup>
$\frac{x_1}{m_1}/\text{mol kg}^{-1}$	$\begin{array}{c} -0.4373 \pm 0.1301 \\ 2.5947 \pm 0.2825 \end{array}$	$-45.2572 \pm 0.8417$	4.0 x 10 -•

USA

### COMPONENTS:

- (1) Mercury; Hg; [7439-97-6]
- (2) Alcohols

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### CRITICAL EVALUATION:

Table 4. The solubility of mercury in 2-propanol. Tentative values of the solubility in concentration, mole fraction and molality as a function of temperature at 0.1 MPa and thermodynamic changes.

Temperature		Mercury Solubility		
t/°C	T/K	Concentration 10°c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction 10° x 1	Molality 10 <sup>6</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
15	288.15	1.6	12.1	2.0
20	293.15	2.1	15.8	2.6
25	298.15	2.67	20.4	3.4
30	303.15	3.4	26.1	4.4
35	308.15	4.3	33.1	5.6
ΔH <sub>1</sub> a		36.3 <u>+</u> 0.3	37.1 ± 0.5	37.6 <u>+</u> 0.7
$\Delta S_1^b$		15.1 <u>+</u> 1.2	$-3.8 \pm 1.6$	$21.6 \pm 2.3$

a units kJ mol<sup>-1</sup> b units J K<sup>-1</sup> mol<sup>-1</sup>

### REFERENCES:

- 1. Reichardt, H.; Bonhoeffer, K. F. Z. Phys. 1931, 67, 780 9.
- 2. Kuntz, R. R.; Mains, G. J. J. Phys. Chem. 1964, 68, 408 10.
- 3. Spencer, J. N.; Voigt, A. F. J. Phys. Chem. 1968, 72, 1913 7.
- 4. Moser, H. C.; Voigt, A. F. USAEC Report 1957, ISC-892, 65 pp.

### ADDENDUM:

A recent paper reports the partition coefficient of mercury between water and octanol-1. The evaluator estimates a solubility of mercury in water saturated octanol-1 (4.6 wt % water) of 1.18 x  $10^{-6}$  mol dm<sup>-3</sup> at 298.15 K. In dry octanol-1 the solubility may be 4 x  $10^{-6}$  mol dm<sup>-3</sup>. See the data sheets and original paper for more details.

- 5. Okouchi, S.; Sasaki, S. Bull. Chem. Soc. Jpn. 1985, 58, 3401 2.
- C. H. Kim and G. K. Vemulapalli (University of Arizona, Tucson) have new measurements in progress on the solubility of mercury in methanol, ethanol, hexane, and 3-methylpentane by atomic absorption. They are also measuring the absolute extinction coefficient of mercury in the solvents.
- 6. Vemulapalli, G. K. private communication.

### COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Methanol or Methyl alcohol; CH<sub>4</sub>O; [67-56-1] CH<sub>4</sub>O; [67-56-1] CARIABLES: CRIGINAL MEASUREMENTS: Reichardt, H.; Bonhoeffer, K. F. Z. Phys. 1931, 67, 780 - 9.

EXPERIMENTAL VALUES:

H. L. Clever M. Iwamoto

Temperature	Mercury Solubility				
t/°C T/Kª	c <sub>1</sub> /mg dm <sup>-3</sup>	Concentration <sup>a</sup> 10 <sup>5</sup> c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10 <sup>s</sup> m <sub>1</sub> /mol kg <sup>-1</sup>	
40 313.15	0.6	0.3	1.2	0.4	
63 336.15	3.6	1.8	7.7	2.4	

<sup>&</sup>lt;sup>a</sup>Calculated by compilers.

T/K = 313.15 - 336.15

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

Some of these results are mentioned in two earlier papers (ref. 1 and 2), but the present paper discusses the solubility work in the most detail.

The solution is analyzed by weighing a gold foil before and after amalgamation with the mercury of the saturated solution. Ultraviolet absorption at 257.15 nm is also used.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. No information given.
- (2) Methanol. No information given.

### ESTIMATED ERROR:

 $\delta c_1/\text{mg dm}^{-3} = \pm (0.1 - 0.2)$ 

### REFERENCES:

- Bonhoeffer, K. F.; Reichardt, H. Naturvissenshaften <u>1929</u>, 17, 933.
- Reichardt, H.; Bonhoeffer, K. F. Z. Electrochem. 1930, 36, 753.

## COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Methanol or Methyl alcohol; CH<sub>4</sub>O; [67-56-1] VARIABLES: T/K = 298.15 CORIGINAL MEASUREMENTS: Kuntz, R. R.; Mains, G. J. J. Phys. Chem. 1964, 68, 408 - 10. PREPARED BY: S. H. Johnson M. Iwamoto H. L. Clever

### EXPERIMENTAL VALUES:

Temperature Mercury Solubility				
t/°C	T/K <sup>a</sup>	Concentration 10°c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup> 10° x <sub>1</sub>	Molality <sup>a</sup> 10*m <sub>1</sub> /mol kg <sup>-1</sup>
25	298.15	1.52	6.19	1.93
2.7	250.25	1.00	3,123	

aCalculated by compilers.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

Spectrophotometric method. It was assumed that the optical density at 2560 A is a reliable measure of the solubility. It was further assumed that the extinction coefficient of mercury was the same in all hydrocarbon solvents. The optical density of a saturated solution of Hg in hexane was measured and, when combined with the solubility measured by Moser and Voigt (ref. 1), gives an extinction coefficient  $s_{2500} = 7.35 \times 10^3 \text{ dm}^2 \text{ mol}^{-1} \text{ cm}^{-1} \text{ at}$ 25°C. The value was used to calculate the solubility in the other solvents.

The Hg and solvent were equilibrated for 20 minutes and the optical density was measured by a Beckman DU Spectrophotometer.

The reliability of the results depends on the Moser and Voigt solubility value in hexane.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. No information given.
- (2) Methanol. Phillips Petroleum Co. Pure Grade hydrocarbon solvent, purified by passage through silica gel until optically pure. Degassed and distilled.

### ESTIMATED ERROR:

### REFERENCES:

 Moser, H. C.; Voigt, A. F. USAEC Report <u>1957</u>, ISC-892, 65 pp.

## COMPONENTS: (1) Mercury; Hg; [7439-97-6]; Mercury-203; 203Hg; [13982-78-0] (2) Methanol or Methyl alcohol; CH<sub>4</sub>O; [67-56-1] VARIABLES: T/K = 288.15 - 308.15 ORIGINAL MEASUREMENTS: Spencer, J. N.; Voigt, A. F. J. Phys. Chem. 1968, 72, 1913 - 7. Voigt, A. F. Personal communication PREPARED BY: S. H. Johnson M. Iwamoto

H. L. Clever

### EXPERIMENTAL VALUES:

Tempe	rature	Mercury Solubility		
t/°C	<i>T</i> /K <sup>a</sup>	Concentration 10°c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10°m <sub>1</sub> /mol kg <sup>-1</sup>
15	288.15	1.7 ± 0.1	6.8	2.1
20	293.15	$2.1 \pm 0.1$	8.5	2.7
25	298.15	2.94 ± 0.09	12.0	3.74
30	303.15	$3.5 \pm 0.1$	14	4.5
35	308.15	4.7 <u>+</u> 0.3	19	6.0

<sup>&</sup>lt;sup>a</sup>Calculated by compilers.

Professor Voigt provided the experimental molar solubility values from J. N. Spencer's research notebook that do not appear in the published paper.

The authors smoothed their data according to the equation:  $\log x_1 = (15.76 \pm .66)\log(T/K) - 45.93$  for the 288.15 to 308.15 temperature interval.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The method and procedure are reported in an earlier paper (ref. 1).

A radioactive tracer method was used. A high activity sample of mercury-203 nitrate was added to mercury(II) nitrate, reduced to metallic mercury by hypophosphorous acid, coagulated into a drop, washed and dried.

The mercury and solvent were shaken continuously in 25 ml glass stoppered volumetric flasks in a thermostat for 24 hours. Aliquots of the equilibrated solution were counted by a conventional single channel scintilation counter. The window width was set to count only the photopeak at 279 kev. The solubility values were the average of at least six determinations over a three day period.

Studies were made to show the solubility of mercury in methanol was not changed by the presence of up to 5 % water. There was no evidence of mercury oxidation during the course of the experiment.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury and Mercury-203. The isotope decays by emission of a beta particle at an energy of 210 kev, accompanied by a gamma ray of 279 kev. The isotope half-life is 47 days.
- (2) Methanol. Fisher Scientific Co. Stated to be 99.9 mol %. Fractionally distilled prior to use.

### **ESTIMATED ERROR:**

 $\delta T/K = \pm 0.1$ ; See random error reported by authors with concentration values above.

### REFERENCES:

Spencer, J. N.; Voigt, A. F.
 J. Phys. Chem. <u>1968</u>, 72, 464.

### COMPONENTS:

- (1) Mercury; Hg; [7439-97-61; Mercury-203; 203Hg; [13982-78-0]
- (2) 2-Propanol or Isopropyl alcohol; C<sub>3</sub>H<sub>8</sub>O; [67-63-0]

### ORIGINAL MEASUREMENTS:

Spencer, J. N.; Voigt, A. F. J. Phys. Chem. 1968, 72, 1913 - 7.

Voigt, A. F. Personal communication

### VARIABLES:

T/K = 288.15 - 308.15

### PREPARED BY:

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### EXPERIMENTAL VALUES:

Tempe	rature	ture Mercury Solubility		
t/°C	<i>T</i> /K <sup>a</sup>	Concentration 10°c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10°m <sub>1</sub> /mol kg <sup>-1</sup>
15	288.15	1.6 <u>+</u> 0.1	1.2	2.0
20	293.15	2.1 ± 0.3	1.6	2.7
25	298.15	2.65 ± 0.07	2.04	3.39
30	303.15	3.4 ± 0.2	2.6	4.4
35	308.15	4.3 ± 0.3	3.3	5.6

aCalculated by compilers.

Professor Voigt provided the experimental molar solubility values from J. N. Spencer's research notebook that do not appear in the published paper.

The authors smoothed their data according to the equation:  $\log x_1 = (15.33 \pm .49)\log(T/K) - 44.61$  for the 288.15 to 308.15 temperature interval.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The method and procedure are reported in an earlier paper (ref. 1).

A radioactive tracer method was used. A high activity sample of mercury-203 nitrate was added to mercury(II) nitrate, reduced to metallic mercury by hypophosphorous acid, coagulated into a drop, washed and dried.

The mercury and solvent were shaken continuously in glass stoppered volumetric flasks in a thermostat for 24 hours. Aliquots of the equilibrated solution were counted by a conventional single channel scintilation counter. The window width was set to count only the photopeak at 279 kev. The solubility values were the average of at least six determinations over a 3 day period.

There was no evidence of mercury oxidation during the course of the experiment.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury and Mercury-203. The isotope decays by emission of a beta particle at an energy of 210 kev, accompanied by a gamma ray of 279 kev. The isotope half-life is 47 days.
- (2) 2-Propanol. Fisher Scientific Co. Stated to be 99 mol %. Fractionally distilled prior to use.

### **ESTIMATED ERROR:**

 $\delta T/K = \pm 0.1$ ; See random error reported by authors with concentration values above.

### REFERENCES:

Spencer, J. N.; Voigt, A. F.
 J. Phys. Chem. <u>1968</u>, 72, 464.

### COMPONENTS:

- (1) Mercury; Hq; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]
- (3) Octanol-1; C<sub>8</sub>H<sub>18</sub>O; [111-87-5]

### ORIGINAL MEASUREMENTS:

Okouchi, S.; Sasaki, S.

Bull. Chem. Soc. Jpn. 1985, 58, 3401-2.

### VARIABLES:

T/K = 278.15 - 308.15 Water saturated 1-octanol.

### PREPARED BY:

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### EXPERIMENTAL VALUES:

	Octanol-l Water Content	Partition Coefficient KOH	Estimated Solubility in Water sat. Octanol-1
T/K	wt %	KON	10°c <sub>1</sub> /mol dm <sup>-3</sup>
278.15	3.7	4.80 ± 0.20	0.76
288.15	4.4	4.75 ± 0.20	1.01
298.15	4.6 ± 0.1	4.15 ± 0.20	1.18
308.15	4.9	3.80 ± 0.20	1.45

Dr. S. Okouchi provided the experimental partion coefficients that did not appear in the original paper.

Values of the water content of octanol-1 were taken from "Alcohols in water", Barton, A. F. M., Editor, Solubility Series 1984, 15, 364 - 7. The same source says water is saturated with  $0.054 \pm 0.005$  wt % octanol-1 at 298 K.

The compiler assumed mercury solubility in water saturated with octanol-1 was the same as the mercury solubility in pure water to estimate the solubility of mercury in the water saturated octanol-1.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

Mercury was dissolved in octanol-1 containing 0.001 mol dm<sup>-2</sup> hydrazine as a reducing agent (ref. 1). Two mL of octanol-1 + mercury and 20 mL of water were shaken together for 214 hours in a thermostated 25 mL centrifuge tube. After equilibration, then centrifugation, the two phases were separated and analyzed by means of cold-vapor atomic absorption (ref. 2).

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Analytical grade, source not given. Purified according to Glew and Hames (ref. 1).
- (2) Water. Doubly distilled.
- (3) Octanol-1. Analytical reagent grade. Distilled twice to remove impurities.

### ESTIMATED ERROR:

### REFERENCES:

- Glew, D. N.; Hames, D. A. Can. J. Chem. <u>1971</u>, 49, 3114.
- Okouchi, S.; Sasaki, S. Bull.Chem. Soc. Jpn. 1981, 54, 2513.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Mercury; Hg; [7439-97-6]	Okouchi, S.; Sasaki, S.	
(2) Octanol-1; C <sub>8</sub> H <sub>18</sub> O; [111-87-5]	Bull. Chem. Soc. Jpn. <u>1985</u> , 58, 3401-2.	
VARIABLES:	PREPARED BY:	
T/K = 298.15	H. L. Clever M. Iwamoto	

### EXPERIMENTAL VALUES:

	Solubility	Concentration	Mole Fraction
<i>T/</i> K	10°01/g cm -3	10°c <sub>1</sub> /mol dm <sup>-2</sup>	107x1
298.15	0.8	4	6

The above values are approximate values that represent a lower limit to the solubility of mercury in 1-octanol. They are based on the author's statement that their stock solution of mercury in 1-octanol was prepared by dissolving approximately 0.8 micrograms of mercury per cubic centimeter of the alcohol.

# METHOD/APPARATUS/PROCEDURE: Mercury was dissolved in octanol-1 containing 0.001 mol dm<sup>-2</sup> hydrazine as a reducing agent (ref. 1). (2) Octanol-1. Analytical reagent grade. Distilled twice to remove impurities. ESTIMATED ERROR: REFERENCES: 1. Glew, D. N.; Hames, D. A. Can. J. Chem. 1971, 49, 3114.